

Pressure-induced amorphization and phase relations in eucryptite

J. Zhang, L. Wang (SUNY at Stony Brook), and T. Uchida (U. of Chicago)
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Introduction: The hexagonal aluminosilicate β -eucryptite (LiAlSiO_4) is a structural derivative of β -quartz (SiO_2) such that half of the $[\text{SiO}_4]^{4-}$ tetrahedra are replaced by $[\text{AlO}_4]^{5-}$ tetrahedra and the charge is balanced by the incorporation of Li^+ into the main structural channels parallel to the c axis¹. β -eucryptite has been of continuing interest to mineralogists due to its structural similarity to quartz. Of particular significance to the field of material sciences is its unusual thermal-expansion properties observed at ambient pressure. As already demonstrated by numerous experimental studies, expansion within the (001) plane of the structure is approximately canceled by contraction along the c axis, yielding negative thermal expansion along the c axis ($\alpha_c \approx -2\alpha_a$) and near-zero volume thermal expansion over a wide temperature range of 300-1400 K²⁻⁵.

The initial objective in a recent study of Zhang et al.⁶ was to examine whether these remarkable thermal-expansion properties in β -eucryptite persist at elevated pressures. During room-temperature compression up to 1.2 GPa, however, β -eucryptite underwent a reversible polymorphic phase transformation to a previously undescribed phase, ε -eucryptite, as referred in the work of Zhang et al.⁶ The primary goal of the present study is to study the stability of β - and ε -eucryptite at higher pressures.

Methods and Materials: The starting β -eucryptite sample was synthesized from Li_2CO_3 , Al_2O_3 , and $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ powders in the molar ratio 1:1:2. The mixture was first sintered at 1373 K for 15 hours and, after regrinding, resintered at 1573 K for 24 hours⁴. X-ray diffraction experiments were performed using a DIA-type cubic anvil apparatus⁷ and a newly developed "T-Cup" high-pressure system⁸. An energy-dispersive x-ray method was employed using white radiation at beamline X17B of the National Synchrotron Light Source and from the bending magnet at beamline 13-BM-D of the Advanced Photon Source. In both experiments, NaCl was used as an internal pressure standard, and temperatures were measured by a W/Re25%-W/Re3% thermocouple. In the course of the experiments, the sample was first compressed at room temperature to 7 GPa in the DIA run and to 13.2 GPa in the T-cup run, followed by heating to the temperature of 1173 K.

Results: Consistent with previous study by Zhang et al.⁶, β -eucryptite was found to transform into ε -eucryptite around 1.2 GPa on room-temperature compression. Upon further compression, amorphization was observed for eucryptite at pressures above 3 GPa, as revealed by the weakening of diffraction intensity and by the continuing growth of diffraction background with increasing pressure. The amorphization, however, did not complete up to 13.2 GPa. On heating at 13.2 GPa, complete amorphization was observed between 523 and 573 K. On further heating, crystalline phases, spodumene and LiAlO_2 spinel, grew at temperatures between 973-1073 K, which were recovered at ambient conditions. For the DIA experiment at 7 GPa, similar outcome was observed when temperature was increased; no complete amorphization, however, was reached before spodumene and LiAlO_2 started crystallizing.

Conclusions: Pressure-induced phase transformations in β -eucryptite is associated with the open nature of its β -quartz-like framework. Open frameworks, however, often become destabilized when pressure is applied, as demonstrated in several studies on zeolites⁹. Amorphization of ε -eucryptite is likely attributed to the fact ε -eucryptite is a metastable phase at pressures above 1.2 GPa⁶. Since direct transformation from ε -eucryptite to spodumene and LiAlO_2 was not observed at our experimental conditions, the present observations can be viewed as one of the classic examples in which an intermediate/metastable phase (usually an amorphous phase) is often involved when transformation between the thermodynamically stable phases is kinetically hindered. Our experimental results show that spodumene and LiAlO_2 spinel are stable phases between 7 and 13 GPa up to 1173 K. In contrast, Ringwood and Reid¹⁰ found that eucryptite adopts a spinel structure at 12 GPa and 1273 K. This discrepancy warrants a further study to clarify phase relations of eucryptite at high pressures.

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